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Urethane Foams From Animal Fats. XI. Urethane Polyols from Epoxidized Tallow, Sorbitol or Trimethylolpropane and Propylene Oxide; Preparation and Properties of Rigid Foams*

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Introduction

Earlier studies at this laboratory established that polyols prepared from tallow-based intermediates could be conveniently used in the formulation of low density polyurethane rigid foams [1,2,3].

In the present work, highly functional polyol mixtures were prepared from the reaction of epoxidized tallow (ET) with sorbitol and propylene oxide (PO). The amounts of reactants, sorbitol and ET, were chosen in terms of their functional equivalent ratios (the ratio of hydroxyl equivalents available from sorbitol to oxirane plus ester equivalents from ET). To introduce fire retardancy, a parallel series of brominated polyols was also prepared. These and other polyols described below were used in formulating free-rise, low, medium, and high density rigid urethane foams. The low density foams reported here were formulated and evaluated essentially by procedures described in earlier publications [4,5]. In addition, medium and high density restricted rise foams were prepared in molds. The foams prepared from the tallow-derived polyols were compared with high density foams formulated with a number of commercially available polyols based on oxyalkylated pentaerythritol, sorbitol, or sucrose.

Earlier investigations demonstrated that tallow-based polyols could be employed in foam formulations for low density applications, but their use in high density foams has not been reported preivously. Generally, the ultimate physical properties of a foam are density dependent. Although the density can be varied within limits by manipulation of the type and quantity of blowing agent, the nature of the reactants are of major importance. Fundamental to the chemistry involved is the equivalent weight and the functionality of the reactants. Increases in functionality and decreases in equivalent weight generally increase the cross-linking density and lead to a denser network a much more rigid foam. The major purpose of this study was to demonstrate that tallow can be modified to give polyols that can be used in high density rigid urethane foam applications.

Experimental Procedure

Materials:

The materials listed below were used as received. tallow, fancy (Mutual-Shoemaker Co., Philadelphia, PA)[1], iodine value 54.8; sorbitol (Andrich Chemical Co., Metuchen, N.J.); propylene oxide (Eastman Organic Chemicals, Rochester, N.Y.); hydrogen bromide, gaseous (Air Products Co., Allentown, Pa.); Triisopropanolamine and Silicone L-530 (Union Carbide Corp., New York, N.Y.); Dabco 33-LV, 33% solution of triethylenediamine in dipropylene glycol; Dabco R-8020, solution of triethylene diamine in dimethyl ethanol amine (Houdry Process and Chemical Co., Marcus Hook, Pa.); Freon-11, trichlorofluoromethane (Matheson Gas Products, New York, N.Y.);

Polymethylene Polyphenylisocyanate, PAPI (Upjohn Co., Kalamazoo, Mich.); Mondur MR (Mobay Chemical Co., Pittsburgh, Pa.); Silicone DC-193 Surfactant (Dow Corning Corp., Midland, Mich.); Dechlorane Plus (Hooker Chemical Co., Niagara Falls, N.Y.); Diethyl N,N-bis(2-hydroxyethyl)aminoethylphosphate, Fyrol-6 (Stauffer Chemical Co., New York, N.Y.); antimony oxide, Thermoguard Antimony Oxide (M & T Chemical, Rahway, N.J.).

Methods

Reaction of Epoxidized Tallow with Sorbitol and Propylene Oxide:

Epoxidized tallow (ET), 250.0 g, (oxirane 3.13% by the Durbetaki [6] method, saponification no. 189.5, acid no. 2.5) and 80.3 g (0.44 mol) of sorbitol, representing a functional equivalent ratio of 2.0, were melted in a 3-necked flask equipped with thermometer, mechanical stiffer, reflux condenser and additional funnel. KOH platelets, 1.65 g (0.03 mol) were added to provide a 0.5% concentration and KOH based on the weight of the mixture. The temperature of the mixture was raised to 160°C, and 128.0 g (2.2 mol) of propylene oxide (PO) was added through the addition funnel under a nitrogen atmosphere at the rate of 0.6 ml per minute. The total reaction time was 4.5 hours. The reaction mixture was then neutralized with concentrated

hydrochloric acid and dried in a rotary evaporator under 0.25 mm pressure. The final product (443.0 g) was an amber-colored liquid containing 2.2 g of KCl. The weight increase, based on the weight of epoxidized tallow, was 77.2%. During the oxypropylation reaction, 112.7 g (1.94 mol) of PO were fixed (0.73 mol of PO per mole of OH from sorbitol). The final product had a hydroxyl content of 10.8%, viscosity (Brookfield) 3,340 cps, at 25C. Thin layer chromatography (TLC) showed no unoxypropylated sorbitol in the product.

Two additional polyols were prepared by the reaction procedure described above, except that the ratio of hydroxyl equivalent from sorbitol to glyceride reactive site equivalents was 4 and 6, respectively. The amount of PO reacted was held constant for all polyols at 0.73 mol PO per mole of OH from sorbitol. The properties of these polyols (A, B, C) are tabulated in Table 1.

Reaction of Epoxidized Tallow With Sorbitol, Propylene Oxide and HBr:

This series of polyols was prepared by the reaction procedure described above except that 102.3 grams (1.76 mol) of PO was added and the total reaction time was 3.5 hours. During the oxypropylation reaction, 77.0 grams (1.33 mol) of PO were fixed (0.50 mol of PO per mole of OH from sorbitol). Hydroxyl content of polyol was 12.0%. TLC showed no unoxypropylated sor-

Table 1. Polyol Properties.

Polyol	Function Equivalent Ratio[a]	Product Composition, Wt%			% Br	Polyol Properties		Viscosity CPS, 25°C
		ET[b]	Sorbitol	PO[b]		Hydroxyl		
						%	Equiv.	
A	2.0	56.5	18.1	25.4	–	10.8	157.5	3,340
B	4.0	39.3	25.3	35.4	–	13.6	125.1	11,480
C	6.0	29.8	29.0	41.2	–	15.7	108.3	23,000
D	2.0	50.5	16.2	15.5	17.8	5.9 (12.0)[c]	288.2	2,150
E	4.0	38.0	24.3	23.1	14.6	9.0 (17.1)[c]	159	4,000
F	6.0	26.7	27.3	26.1	19.9	8.0 (18.9)[c]	212.6	6,500

(a) Moles OH/moles (oxirane + ester).

(b) ET = epoxidized tallow; PO = propylene oxide.

(c) OH content before bromination.

Table 2. Rigid Foam Formulations (Parts by Weight).

	Low[b] Density	Medium[b] Density	High[c] Density Molded
Epoxidized tallow-sorbitol-propylene oxide polyol[a] (OH No. 518; OH Equiv. 108)	8.70	-	-
Epoxidized tallow-sorbitol-propylene oxide polyol (OH No. 356; OH Equiv. 157.5)	-	40.0	528.8
Triisopropanolamine (OH No. 850; OH Equiv. 66)	1.30	-	-
Triethylenediamine (Dabco 33-LV)	0.25	-	-
Triethylenediamine (Dabco R-8020)	-	0.4	1.9
Water	-	0.16	1.06
Trichlorofluoromethane (Freon-11)	4.10	-	-
Polymethylene Polyphenylisocyanate (PAPI) (105 index)	13.80	-	-
Polymethylene Polyphenylisocyanate Mondur MR (105 index)	-	37.8	501.2
Silicone L-530 Surfactant	0.16	-	-
Silicone DC-193 Surfactant	-	0.4	5.3

(a) Equiv. wt. adjusted to 100 with triisopropanolamine.

(b) Unrestricted rise.

(c) Restricted rise.

bitol in the product. Bromination was carried out as follows: the temperature of the mixture (406.7 grams) was reduced to 70C; nitrogen flow was stopped, and a Dean-Stark water trap was attached. Benzene, 41 grams, was added, and the mixture was then heated and stirred at 120C. Gaseous hydrogen bromide, 127.0 grams (1.57 mol), was bubbled through the reaction mixture at the rate of 21.2 grams (0.26 mol) per hour. After six hours reaction, 30.0 grams of water was collected. The solvent was removed from the mixture on a rotary evaporator under 0.25 mm pressure. Potassium bromide (3.6 grams) precipitate was separated by decantation. The final product (450.0 grams) was a dark brown liquid at room temperature, hydroxyl content 5.9%, bromine 17.8%, and viscosity (Brookfield) 2,150 cps at 25C. This product mixture was used without further modification. As in the series described above, the number of hydroxyl equivalents from sorbitol to those from the glyceride reaction sites was varied. Ratios of 2, 4, and 6 equivalents were used. The properties of these polyols (D, E, F) are given in Table 1.

Foam Preparation and Testing

Low Density Unrestricted Rise Foams:

A typical formulation for the low density free-rise (unrestricted) foams is given in Table 2. A one step procedure was used in the preparation. A well stirred mixture of the polyol (adjusted to an equivalent weight of 100 or 120 with triisopropanolamine or used without adjustment of equivalent weight), catalyst and blowing agent was added to a mixture of the crude polymeric isocyanate (AE 105) and silicone surfactant. The resultant blend was then stirred with a Conn blade affixed to a drill until the onset of creaming and then poured into a 9 oz. paper cup. Foaming was generally complete within 100 seconds. After curing at room temperature for one week, the foams were cut and tested. Two additional series of foams were prepared from these polyols. In one series, a combination of nonreactive fire retardants, Sb_2O_3 and Dechlorane Plus, were used at 15% and 30% (w/w) based on weight of polyol mixture. In the other series, a reactive phosphorous containing

Table 3. Formulations Containing Reactive and Nonreactive Fire Retardants (Parts by Weight).

Component	Polyol Equiv. Wt.	Formulation No.			
		1[b]	2[c]	3[d]	4
Polyol A	157.5	--	--	5.5	--
Polyol B	125.1	5.9	7.8	--	--
Polyol E	189	--	--	--	10[e]
TIPA[a]		4.1	2.2	3.5	--
Triethylenediamine (Dabco 33-LV)		0.25	0.25	0.25	0.25
Trichlorofluoromethane (Freon-11)		4.1	4.1	4.1	4.1
Polymethylene Polyphenylisocyanate (PAPI)		14.0	11.7	11.1	7.2
Silicone L-530 Surfactant		0.16	0.16	0.16	0.16
Dechlorane Plus		3.0	3.0	--	--
Sb_2O_3		1.5	1.5	--	--
Fyrol-6		--	--	3.0	--

(a) Triisopropanolamine.

(b) At equiv. wt. = 100

(c) At equiv. wt. = 120

(d) At equiv. wt. = 125

(e) Polyol E contains 14.6% bromine.

retardant additive, Fyrol-6 (equivalent weight 128.3), was used. Typical formulations are given in Table 3.

Medium and High Density Unrestricted Rise Foams:

Table 2 gives a typical formulation for the medium density free-rise foams prepared. To a mixture of the polyisocyanate and silicone surfactant contained in a paper cup was added a mixture of the polyol, catalyst, and water. The blend was stirred until the onset of creaming (about 20 seconds) with a heavy duty Conn blade affixed to a drill. For the higher density foams the amount of water was halved over that shown in Table 2 for the medium density foams. Again all foaming was allowed to take place unrestrained in a 9 oz. paper cup. The tallow based polyols were used directly without adjustment in equivalent weight.

Molded Restricted Foams:

A three-sided square aluminum mold having a mold cavity 7-in.² by 3-in. high was designed and constructed from 3/8-in. aluminum plate. The top surface plate, with 1/8-in. holes drilled and spaced 2-in. apart, was mounted to the rest of the assembly through fixed bolts and fastened with wing nuts.

A quantity, sufficient to give a precalculated density (12 and 24 lbs/ft³), of the thoroughly blended foam mixture was poured under ambient conditions into the open mold just prior to the onset of creaming. The cover was secured to the mold, and foaming was allowed to proceed. Loading was parallel to the 3-in. dimension of the mold (horizontal pour). After 30 minutes the mold was opened and the foam was allowed to cure under ambient conditions for one week. A typical formulation is given in Table 2.

Test Methods:

Density, Procedure ASTM D 1622-59T; comprehensive strength, Procedure ASTM D1621-59T, using an Instron Tensile Tester with reversed cage attachment, operated at a cross-

head speed of 0.1 in/min.

Flexural strength was determined by ASTM 790-66. Dimensional stability with humid aging was performed as described by the procedure of Seefried [8].

The relative flammability characteristics of the foams were evaluated using ASTM Method D 1692 modified for convenience. A small sample, 50 mm long, 37 mm wide, and 13 mm high, marked 10 mm from each end, was supported horizontally upon a metallic screen clamped to a ring stand. A microburner, whose flame height was adjusted so that the uppermost edge would just impinge on one end of sample, was employed as the flame source. The flame was brought in contact with the sample and permitted to remain there for 30 seconds or until the flame first reached the first 10 mm mark, and then removed. The relative flammability characteristics of the foams were evaluated by determining the burning rate and % area burned. The cause for extinguishing was also noted. These data were useful only for comparative purposes and are not meant to convey flammability of foam under actual condition of ignition. Flammability was rated complete if the sample burned beyond the second mark (40 mm from ignited edge) after removal of flame source.

Results and Discussion

Polyol Synthesis:

Under the conditions employed, a variety of reactions take place simultaneously. As explained below, our earlier works indicated that the more probable course is reaction of partially or totally propoxylated sorbitol with the oxirane groups of ET, to give fatty hydroxy ethers of sorbitol. Approximately 14% of the ET consists of fully saturated triglycerides and does not contain any oxirane group. Reaction of propoxylated sorbitol with glyceride linkages provides a mixture of products including diglycerides, monoglycerides, and esters of sorbitol. The simplicity of using only one catalyst (KOH), instead of two (KOH, BF₃) in two stages as previously reported by this laboratory [9], is an obvious advantage. The KOH catalyst used in this procedure effectively catalyzed the alcoholysis reaction and oxypropylation of hydroxyl bearing components [10]. The resulting polyols possess secondary hydroxyl groups predominantly and therefore react at lower more convenient rates with an isocyanate-terminated prepolymer to form urethane foams with modified properties. Since the internal oxirane groups of ET are less reactive than those of PO, in the above reaction the oxypropylation of sorbitol probably comes first followed by

alcoholysis of both oxirane and ester groups of ET.

Foams:

Low, medium, and high density rigid foams were prepared from the polyols described by use of a commercial blowing agent, trichlorofluoromethane (low density formulations), and carbon dioxide (high density formulations) generated by reaction of water with diisocyanate. The medium and high density foams were prepared under conditions of restrained and unrestrained (free) rise and the low density foams only under unrestrained rise conditions. The specific formulation used for preparing foams in each category is described separately. Except where noted, for a direct comparison of the foam from each series, the formulating conditions were kept essentially identical. The design of a formulation depends on the specific end use intended for the cellular product. Similarly, the physical tests selected to evaluate a material also depend on the ultimate design and the particular requirements for the material. The tests classically used in evaluating higher density cellular foams intended for use in plaques and furniture are surface and fracture impact durability, dimensional stability at elevated temperatures, screw holding strength and flexural properties.

Table 4. Properties of Low Density Foams.

Polyol	OH Equiv.[c]	Density lbs/ft³	Comp. str.[d,e] psi	Comp. Mod psi
A[a]	157.5[f]	1.6	23	580
	120	1.8	30	720
	100	1.9	24	725
B[a]	123.1[f]	1.7	25	650
	110	1.7	30	800
	100	1.9	38	840
C[a]	108.3[f]	1.8	38	915
	100	1.8	38	925
C[b]	169.7[f]	1.6	22	570
	120	1.7	25	650
	100	1.8	28	700

(a) Polyol source: epoxidized tallow + sorbitol + PO.

(b) Polyol source: epoxidized tallow + trimethylolpropane + PO.

(c) Adjusted with triisopropanolamine (TIPA).

(d) Parallel to rise.

(e) 10% compression.

(f) No adjustment of equiv. wt.

These are the physical propeties most sensitive to formulation variations and are most meaningful in a comparative evaluation. Since the formulations reported here were arbitrarily selected, the data presented may not necessarily represent the best attainable and are useful only for comparative purposes. It was not within the scope of this study to establish optimum foam formulations. The experiments were designed to determine if fat-based polyols were suitable for use in producing rigid urethane foams. Values for both free and restricted rise foams are reported.

Table 4 gives a summary of the physical properties of the low density foams formulated from the nonhalogenated polyols A, B, C prepared from epoxidized tallow, sorbitol, and propylene oxide. For comparison, the table also includes the physical properties of a low density foam prepared from a polyol which was reported in a previous publication [9]. This polyol (G) consisted of a mixture resulting from the reaction of epoxidized tallow, trimethylolpropane, and propylene oxide. Details for its preparation were similar to those described in this previous publication. In general, as the equivalent weights of the polyols decreased, the densities, compressive strengths, and moduli of the resulting foams increased. This is also evident in the foams prepared from these polyols when the equivalent

weights were adjusted to 100 and 120 (generally required in low density formulations containing fat-based polyols since the equivalent weights of the fatty polyols are too high to allow sufficient cross-linking to give foams of acceptable dimensional and strength properties [11]) with triisopropanolamine. At similar equivalent weights, the physical properties of the foams from the sorbitol polyol A were similar to those derived from the trimethylolpropane polyol G (equivalent weights of 157.5 and 169.7, respectively); at adjusted equivalent weight of 100 and 120, the compressive strengths and moduli of the foams prepared from polyols A, B, and C were higher than those prepared from polyol G. These higher values apparently were due to the higher functionality contributed by the sorbitol polyols.

Satisfactory foams could not be formulated from the brominated sorbitol polyol directly without adjustment of the equivalent weights. Severe shrinkage resulted. Therefore, only the polyol mixtures adjusted to equivalent weights of 100 and 120 with triisopropanolamine could be conveniently evaluated in low density rigid foams (Table 5).

The foams formulated from the brominated polyols all had higher densities but lower strengths than those prepared from the unbrominated polyols. The higher densities pro-

Table 5. Properties of Low Density Foams From Halogenated Polyols.

| Polyol[a] | OH Equiv.[b] | Density lbs/ft^3 | Comp. Str.[c,d] psi | Comp. Mod. psi | Percent bromine | | Ignition Test[e] |
					Polyol	Foam	
D	288.2	(Severe shrinkage)			17.8	--	
	120	2.0	31	845	--	10.3	Burned completely
	100	2.0	35	910	--	7.8	" "
E	189	(Severe shrinkage)	---		14.6	--	
	120	1.9	21	575	--	10.2	Burned completely
	100	1.9	26	780	--	7.5	" "
F	212.6	(Severe shrinkage)	---		19.9	--	
	120	1.8	24	560	--	13.0	Ignition inhibited
	100	1.9	28	675	--	9.8	" "

(a) Polyol source: epoxidized tallow + sorbitol + propylene oxide + HBr.

(b) Adjusted to 120 and 100 with triisopropanolamine.

(c) Parallel to rise.

(d) 10% compression.

(e) Modified ASTM Method D 1692 as described in text.

Table 6. Burning Properties of Low Density Foams Formulated with Retardants — Unhalogenated Polyols

Polyol Source	OH Equiv.	Density lbs/ft^3	Retardant	Burning Rate[d] Cms/m	% Area Burned[e]	Comp. str. psi	Comp. Mod. psi
A	157.5	2.0	Dechlorane Plus Sb$_2$O$_3$ [b]	2.85	28.5	21	707
	120[a]	2.1	"	2.55	25.5	27	830
	100[a]	2.1	"	1.85	18.5	26.5	933
	100	1.9	Fyrol-6[c]	2.25	22.5	37	1030
B	125	1.8	Fyrol-6[c]	2.30	23.0	27	775
	120[a]	2.0	Dechlorane Plus Sb$_2$O$_3$ [b]	2.55	25.5	27.5	943
	100[a]	2.1	"	3.02	30.0	30.5	915
	100	2.0	Fyrol-6[c]	2.85	28.5	39.5	913
C	108.3	2.1	Dechlorane Plus Sb$_2$O$_3$ [b]	2.40	24.0	29.5	978
	100.0[a]	2.0	"	2.25	22.0	30	863
	100.0	1.8	Fyrol-6[c]	2.40	24.3	34.5	823

(a) Adjusted with triisopropanolamine (TIPA). (b) 2:1 Ratio @ 30% of total polyol wt.
(c) At approx. 30% of polyol wt   (d) Modified ASTM Method D 1692 as described in text.
(e) Burning extinguished by char formation.

bably were due to the greater amount of triisopropanolamine which had to be added to the brominated resulted in lower compressive strengths than would be predicted for thse higehr density foams but did not impart satisfactory flammability characteristics.

The physical proerties of foams formulated with fire retardant additives are given in Tables 6 and 7. Two types of additives were evaluated, a reactive Fyrol-6, and nonreactive, either Dechlorane Plus and Sb$_2$O$_3$ or Sb$_2$O$_3$ alone. The addition of either additive resulted in a marked improvement in fire retardant properties of the foams, with no great difference in the degree of retardancy between the various types of retardants.

The use of nonreactive retardant in the formulations resulted in higher densities than noted for the same foams prepared without additive (Tables 4 and 5). Although the compressive strengths, compared to those of the foams without retardant, were somewhat lower than

would be expected at the higher densities, there was generally a gain in the compressive moduli. These same trends were evident with the foams formulated with the reactive retardant. This may suggest that the fat-based polyols may be contributing some plasticizing properties to the foam, thereby improving its additive carrier property with little or no loss in physical properties.

In the foams formulated with the halogenated polyols D, E, and F only the nonreactive retardant Sb$_2$O$_3$ was evaluated. The addition of Sb$_2$O$_3$ resulted in a significant improvement in fire retardancy, but this was accomplished by a loss in compressive strength. The compressive modulus appeared to be unaffected.

The results of the evaluation of the polyols in medium and high density foams are given in Table 8. Shown for comparison are corresponding data for foams prepared from sorbitol derived polyols, from four commercial polyols, and from three TMP-ET-based polyols [12, 13] which had not been evaluated in medium and

Table 7. Burning Properties of Low Density Foams Formulated with Retardants — Halogenated Polyois.

Source	OH Equiv.	Density lbs/ft^3	Retardant	% Br In Original Polyol	% Br In Final Form	Burning Rate[c] cms/s	% Area burned	Comp. str.[k] psi	Comp. Mod. psi
D	120[a]	2.0	b	17.8	4.0	Complete	--	21	845
	100[a]	2.0	b	17.8	2.8	Complete	--	25	910
	120[a]	2.3	Sb_2O_3[c]	17.8	3.6	6.0[d]	30[e,i]	25.5	768
	100[a]	2.2	Sb_2O_3[c]	17.8	3.5	6.3[e]	31[f,i]	28	905
E	120[a]	1.9	b	14.6	3.9	Complete	--	21	575
	100[a]	1.9	b	14.6	2.7	Complete	--	26	780
	120[a]	2.2	Sb_2O_3[c]	14.6	3.5	3.3	33[f]	18	605
	100[a]	2.0	Sb_2O_3[c]	14.6	2.5	4.7	31[f]	20	593
F	120[a]	1.8	b	19.9	5.0	6.6	57[j]	24	560
	100[a]	1.9	b	19.9	3.4	6.4	52[j]	28	675
	120[a]	2.1	Sb_2O_3[c]	19.9	4.5	2.3	23[g,i]	18	575
	100[a]	2.0	Sb_2O_3[c]	19.9	3.1	2.0	20[h,i]	20	676

(a) Adjusted with triisopropanolamine.
(b) No additional flame retardant additive to that of bromine present in polyol originally.
(c) Ratio of retardant: fatty polyol of 1:2.
(d) Modified ASTM Method D 1692 as described in text.
(e) No further burn through after 1.5 cm burn through in 15 secs.

(f) No further burn through after 1.6 cm through in 15 secs.
(g) No further burn through after 11.5 cm through in 15 secs.
(h) No further burn through after 10 cm burn through in 15 secs.
(i) Burning extinguished by chain formation.
(j) Burning extinguished by gaseous atom.
(k) 10% compression.

Table 8. Properties of Medium and High Density Foams (Unrestrained Rise).

Polyol	OH Equiv.	Density lbs/ft	Comp. str. psi	Comp. Mod. psi	Flex str. psi	Flex Mod. psi
A	157.5	12.3 / 20.3	237 / 995	8340 / 23488	200	4725
B	125.2	13.6 / 21.6	497 / 1233	12750 / 29055	215	7425
C	108.3	16.5 / 22.3	740 / 1370	17675 / 32000	465	10340
D	288.2	10.7 / 16.8	85 / 140	2555 / 4100	-	-
E	189	10.7 / 14.8	248 / 410	3709 / 12700	-	-
F	212.6	11.2 / 15.0	290 / 475	10093 / 14132	-	-
TA[a]	270	12.5 / 18.2	195 / 395	6093 / 10880		
TB[a]	227	13.5 / 19.2	300 / 555	9385 / 14785		
TC[a]	175.3	14.1 / 19.8	432 / 925	12033 / 21310		
CA[b]	148.3	11.9 / 15.5	313 / 500	8970 / 14717		
CB[b]	153.2	12.1 / 15.1	350 / 540	10855 / 14982		
CC[b]	168.6	9.4 / 20.8	223 / 1087	6858 / 30230		
CD[b]	132	8.4 / 10.3	168 / 235	4865 / 7120	120	2842

(a) Polyol source: ET + TMP (excess TMP washed out with H_2O).
(b) Commercial polyols: sorbitol/pentaerythritol/sucrose + PO.

Table 9. Burning Properties of Medium and High Density Foams Prepared from Brominated Polyols.

Polyol	OH Equiv.	Density	% Bromine in Foam (w/v)	Burning rate[b] cms/m	% Area[d,e] Burned in 30 sec.
D	288.2	10.5 / 16.8[a]	9.7 / 15.5	3.2 / -	32 / -
E	189	11.2 / 14.1	9.3 / 11.7	1.0 / 0.7	10 / 7
F	212.6	10.9 / 15.0	11.5 / 15.8	2.3 / 1.0	31[c] / 10

(a) Insufficient material to allow for adequate sample for burning test.
(b) Flame arrest caused by char and gas formation.
(c) Smaller sample used in test.
(d) Modifies ASTM Method D 1692 as described in text.
(e) Burning extinguished by char formation.

high density formulations. All polyols were used without adjustment of the original equivalent weight.

The sorbitol based polyols A, B, and C and the TMP-based polyols TA, TB, and TC gave foams with similar densities, although the OH equivalents were considerably higher for the latter series than for the former. If physical proper-

ties were solely density dependent, compressive strengths would be expected to be similar at equal densities. This was not observed in the two series. Instead, the compressive strengths and moduli were more dependent upon the equivalent weights of the polyols. The medium and high density foams from the sorbitol polyols, with lower equivalent weights, had higher compressive strength and modulus values than those from TMP polyols, with higher equivalent weights. The higher compressive strengths of the foams from the sorbitol polyols may be due to the higher functionality of these polyols, leading to increased cross-linking, a denser network, and greater rigidity. The higher equivalent weights of the TMP polyols result in polymers with fewer cross-links per unit volume and lower cross-link densities and hence foams with lower compressive strength and modulus.

Within each series, as the equivalent weight was increased, the density decreased, as did the corresponding compressive strength and modulus. Within a given series, then, the generalization that properties are density dependent is valid.

Table 8 also shows that the fat-based polyols, at comparable equivalent weights, yielded foams that were equal or superior to the commercial polyols in compressive strengths and moduli. Furthermore, the higher density foams prepared from the halogenated fat-based sorbitol polyols D, E, and F had compressive strengths and moduli much lower than those of the foams prepared from similar polyols which did not contain halogen.

The burning characteristics of medium and high density foams made from halogenated polyols are given in Table 9. Since the percent of halogen in final form is proportional to the density (w/v), the higher density foams had a greater degree of retardancy. Nevertheless, even in the higher density foams the level of retardancy was unsatisfactory. The addition of an additive such as Fyrol-6 or Sb_2O_3 should result in improved nonburning character. Since sorbitol has excellent char forming characteristics, the results of the burning tests reported here were unexpected, considering that the polyols contained a large percentage of sorbitol. This charring effect of sorbitol was probably offset by the inherent burning characteristics of the higher proportion of fatty acid in the polyol mixture.

Molded Foams:

The physical properties of molded foams are given in Tables 10 and 11. All measurements were taken parallel to the direction of rise from the core of blocks with skin removed. At lower densities, measurements taken in the direction of rise gave much higher values than those

measured perpendicularly to this direction, but, as density increased the difference between the two directions became smaller. This difference was due to the anisotropy of the cells making up the low density foams, the cells being elongated in the direction of the rise. As the density of the resulting foam begins to exceed 8 pcf, the cells are packed together and become more isotropic, and the values obtained from perpendicular and parallel measurements become equal. Shown in Table 10 is the density of molded foam with skin intact, density of core, compressive and flexural strengths and moduli. Tables 10 and 11 include the physical properties of molded foams formulated from polyol G mentioned above, from a second polyol G_1 similarly prepared from epoxidized tallow, trimethylol propane and propylene oxide, but at a different equivalent weight, and, for comparative purposes, from commercial polyols CA through CD.

The compressive and flexural strengths and the moduli of the foams prepared from the bat-based polyols A, G, and G_1 compared favorably with or were superior to those of the foams prepared from the commercial polyols CA through CD at both density levels studied. For foams prepared from fat-based polyols, a two-fold increase in density was accompanied by a three- to four-fold increase in compressive strength, although the modulus rose only two-and-one-half to three-and-one-half fold. For the same increase in density, the flexural strength and modulus increased approximately three-fold. Comparison of physical properties of the foams formulated from the fat-based TMP polyols G and G_1 shows that the polyol with lower equivalent weight, G_1, gave higher compressive and flexural values at both levels of density. The higher functional sorbitol polyol A has an equivalent weight midway between those of

Table 10. Physical Properties of Molded Foams.

Polyol	OH Equiv.	Density (lbs/ft³)		Comp. Str. psi	Comp. Mod. psi	Flex Str. psi	Flex. Mod. psi
		Block[a]	Core				
A	157.5	12.3	11.2	294	9348	225	2955
		23.7	21.4	696	25249	735	9365
G	169.7	11.5	10.2	188	4489	245	3260
		21.3	19.0	515	12920	595	7725
G_1	147	13.1	11.0	243	9024	245	3350
		22.6	19.4	528	22474	690	9525
CA	148.3	12.4	10.3	178	4398	275	2800
		23.9	20.7	590	13583	660	8460
CB	163.2	11.7	10.3	176	4415	210	2825
		24.7	21.6	730	15780	765	9936
CC	168.4	12.4	10.4	259	5438	280	3545
			20.3	654	15515	670	8715
CD	181.7	12.8	10.2	146	3759	200	2810
		21.3	19.4	515	14470	585	7650

(a) Density of block - skin intact.

(b) Average density of samples with surface skin removed.

(c) Parallel to rise - 10% compression.

Dimensional Stability with Humid Aging[a,b]

Polyol	OH Equiv.	Density[c] (lbs/ft³)	Vol Δ %	Compressive Str. (psi)		Density After Humid Aging (lbs/ft³)	Screw Torque	
				Before Humid Aging	After Humid Aging		Density (lbs/ft³)	Torque (in/lbs)
A	157.5	-	-	-	-	-	11.6	4.6
							21.6	19.2
G	169.7	10.6	1.25	190	293	10.9	11.0	6.3
		19.1	1.19	628	705	19.4	19.4	18.3
G₁	147	-	-	-	-	-	11.4	5.1
							20.1	19.2
CA	148.3	10.3	1.74	188	258	10.5	10.5	5.5
		20.9	0.26	663	875	21.1	20.9	18.0
CB	153.3	10.5	1.23	200	245	10.5	10.4	4.9
		21.9	2.22	808	1020	22.2	22.2	19.3
CC	168.8	10.5	-1.36	213	285	10.8	10.6	5.8
		19.6	-0.13	610	940	20.1	21.3	19.5
CD	181.7	10.4	-0.80	153	170	10.8	10.6	6.0
		19.3	-0.80	585	735	20.3	19.7	17.1

(a) 78°F, 100% relative humidity for 7 days.
(b) Values given are average of samples from top and bottom section of core.
(c) Density before humid aging less than after HA. The comp. str. values reflect this difference. This density increase may be due to trapped water.

the TMP polyols G and G₁. However, the foams obtained from polyol A gave higher compressive and flexural strength and compressive modulus values than those from polyols G and G₁. This is as expected, since the sorbitol polyol A is more highly functional than the TMP polyols G and G₁.

The results of dimensional stability with humid aging, reported in terms of percent volume change, and compressive strength before and after humid aging, and screw torque are shown in Table 11. Generally, a high humidity tends to plasticize a foam with a resulting loss in strength; therefore, these data were obtained to determine the effect of humidity on the foams prepared from the fat-based polyols. For these polyols to have merit, their dimensional stability and strength must be no more affected by humidity than are those of foams prepared from the commercial polyols. The humid aging data must be interpreted according to the maximum allowable expansion or shrinkage, in most defense foam applications generally 2% less in linear dimension, and whether the foam returns to its original strength when the moisture is removed. The data reported are within the acceptable limits for each of these two criteria. Fur-

Table 12. Screw Torque vs Density.

Density (lbs/ft³)	Screw Torque (in/lbs)
5.3	1.8
11.4	5.1
15.1	8.3
20.1	19.2

ther, these fat-based foams compared favorably with and were either equal or superior to those made from the commercial polyols.

The torque required to strip the screw threads in the foam was, as expected, density dependent. For the fat-based foams this value varied between 4.6 and 6.3 in lbs for densities of approximately 11 lbs/ft³ and between 18.3 to 19.2 for the higher density foams. These values were equal or superior to those noted for the commercial foams. The density dependence of this physical property is illustrated in Table 12 and Figure 1.
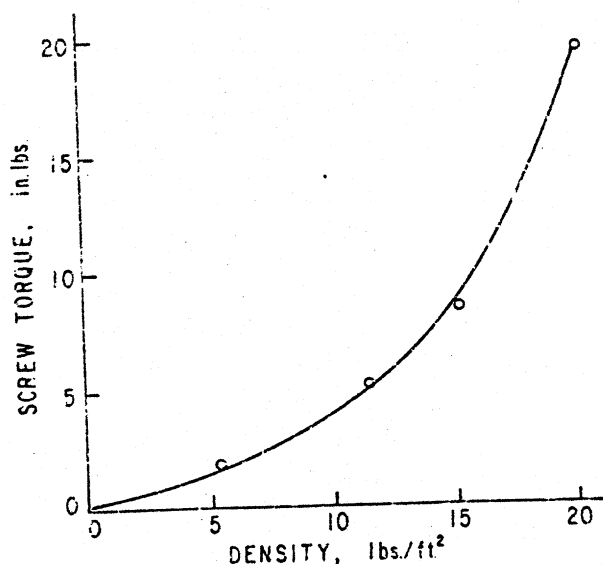
Figure 1. Screw Torque Vs. Density.

Conclusions

These investigations demonstrate that a renewable agricultural resource, tallow, can be readily modified to give intermediates suitable as polyol components in formulations for urethane foams. The degree of functionality can be varied by the proper choice of reactants. Typical syntheses illustrating the modifications of tallow to give highly functional polyols are outlined. The preparation of low, medium, and high density rigid foams from these tallow-based polyol intermediates is described. Data obtained on physical properties for the dense foams prepared suggest that the use of these intermediates is feasible in the manufacture of nonsupportive furniture and plaques. The study also indicates that the formulations containing these fat-based intermediates can tolerate sufficient selected fire retardants for noticeable reduction of the burning characteristics of the resultant foams.

Acknowledgement

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